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METAL DUSTING RESISTANT PRODUCT

FIELD OF THE INVENTION

5 The present invention relates to products that are resistant or immune to carburization, metal dusting and coking, and resistant to oxidation, and that furthermore have sufficient mechanical strength for use at temperatures greater than 400°C and at high pressures and that have the ability to retain the resistance or immunity to the above mentioned corrosion types even for longer
10 periods of time. The invention is also related to the use of said product in the construction of components in CO-containing atmospheres, and/or hydrocarbon-containing atmospheres or solid-carbon-containing processes.

BACKGROUND OF THE INVENTION

15 Developments of the reforming processes in the petrochemical industry during the last years have led to significant process efficiency improvements. One such example is the development of large pore zeolite catalysts, doped with specific metals, rendering the catalysts with a high selectivity, which makes
20 them suitable for precision reforming and/or —synthesis. This allowed more effective and economic production of a range of highly demanded commercial liquids based on hydrocarbon feedstocks. However, the catalysts were soon discovered to be sensitive to sulfur poisoning. In order to overcome this disadvantage techniques to desulphurize the hydrocarbon feed have been
25 developed. Later, such catalysts were also found to be quickly deactivated by water, thus corresponding protecting technologies to lower the water content in the process gas streams were developed.

The low-sulfur and low-water conditions led to the discovery of coke-formation and plugging within reactor systems; an effect which later was found to relate
30 back to a severe form of disintegrating attack on metallic construction materials, which affects parts of the equipment such as furnace tubes, piping, reactor walls strongly negative by e.g. shortening the service time of the whole plant.

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This metal disintegrating mechanism was already known since the 1940's as so-called "metal dusting". The metal dusting process is known to be inhibited by the presence of sulphur in the carbon containing gas. Increased environmental demands and the requirements of newly developed catalysts have made low-sulphur conditions necessary, which has led to an increase in metal dusting related failures.

As earlier mentioned, metal dusting is a form of catastrophic carburisation, where the metal disintegrates rapidly into coke and pure metal or other types of metal rich reaction products. Metal dusting is in the present case taken to mean the process whereby a metal or an alloy is attacked by a carbon rich gas and corroded into a mixture of coke/carbon and metal rich particles. Metal dusting typically occurs in gases that are initially supersaturated with respect to carbon, i.e. having a carbon activity greater than unity. The corrosion products of the metal dusting process are metal rich compounds and carbon rich compounds. The carbon rich compounds are typically in the form of coke, i.e. a solid carbonaceous deposit that can contain varying concentrations of e.g. hydrogen, nitrogen, oxygen etc. The metal rich compounds can be different depending on e.g. the oxygen content of the system and the alloy composition, as well as the operating temperature and pressure. Typical metal rich compounds are metal carbides, metallic alloys with dissolved carbon and oxides of the component metals in the alloy.

Metal dusting occurs most commonly when a carbon containing gas is cooled from a high temperature at which it is at or near equilibrium. Often this equilibrium state is reached with the help of catalysts, which means that at the initial equilibrium, the gas phase reaction rates are low. During cooling, the gas will not be able to equilibrate, due to sluggish kinetics, and as a consequence the gas becomes strongly carburising. In most applications where metal dusting is a problem, such as for example in steam reforming applications processes, the gas is cooled in order to retain the equilibrium achieved at high temperature over a catalyst. It is thus a necessary feature of such processes that metal dusting can occur, and it is not possible to design the process so as

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to avoid metal dusting, carburisation or coking entirely. According to P. Szakalos, "Mechanisms of metal dusting on stainless steel", Licenciate thesis, 2002, ISBN 91-7283-260-6 metal dusting is thus likely to occur in those components where the gas is cooled, such as waste heat boiler, steam superheaters and in heat exchange reformer units. The temperature range in
5 which metal dusting is most likely to occur is 400-800°C.

The atomised metal particles produced by metal dusting can be transported with the process gas, accumulate downstream on various reactor parts, and
10 throughout the whole reactor system, metastasise catalytic coking that can create blockage.

It is generally appreciated that metal dusting is a large concern in the production of hydrogen and syngas (H_2/CO mixtures). In these plants, methane and various other higher hydrocarbons are reformed or partially oxidised to produce
15 hydrogen and carbon monoxide in various amounts for use in producing other higher molecular-weight organic compounds. Increased reaction and heat-recovery efficiencies of the processes necessitate operating process equipment at conditions that favour metal dusting.

The need for increased heat recovery in ammonia-synthesis processes has
20 caused metal dusting problems in the heat-recovery section of the reformed-gas system as well as in the reformer itself.

Metal dusting is also a problem in direct iron-ore reduction plants wherein reformed methane is dried and reheated to enhance ore-reduction efficiencies. Metal dusting occurs in the reformer, reformed-gas reheater and piping up-
25 stream of the ore-reduction.

Metal dusting is also experienced in the heat-treating industry in equipment that handles items being treated (annealed, carburized).

Gases used in heat treating mix with oil residue on the items to form gases that are chemically favourable for metal dusting.

30 Gas mixtures used for carburizing can also cause metal dusting if control of chemistry of the process is not taken care of.

Petroleum refineries experience metal dusting in processes involving hydro-dealkylation and catalyst regeneration systems of "plat-former" units.

Other processes wherein metal dusting occurs are nuclear plants that employ carbon dioxide for cooling the equipment in the recycle-gas loop of coal-gasification units, in fired heaters handling hydrocarbons at elevated temperatures, iron-making blast furnaces in steel mills, and fuel cells using molten salts and hydrocarbons.

In recent years, there has been a strong emphasis on reforming and synthesis technology developments to make possible commercialisation of remotely located, so-called "stranded gas reserves". The synthesis step, based on further developments of the Fischer-Tropsch process, will require the use of highly severe metal dusting causing compositions of the synthesis gas, with lower steam to carbon ratios and higher CO/CO₂ ratios, which will cause severe metal dusting. However, only small steps in the development in this direction have been taken due to lack of material with sufficient resistance to metal dusting.

DESCRIPTION OF THE RELATED ART

The solutions that are used nowadays in order to provide protection to metal dusting and reduce the formation of coke is to use advanced nickel- or iron-base alloys with high contents of chromium and certain additions of aluminium. Several methods of surface modification, which are based on diffusion coating techniques or coatings by overlay welding, laser fusion, chemical vapor deposition (CVD), physical vapor deposition (PVD) or sputtering have been tested. Many of those methods include elements based on transition metals, such as iron, nickel and cobalt, which are known for their catalytic properties referencing to their promotion of coke formation.

There are metals, such as Cu and Sn, which are known to be resistant or immune to carburization and coke formation. Sn has a too low melting point to be useful above 300°C and both Cu and Sn have insufficient oxidation resistance for use in high temperature applications. This oxidation resistance is

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required in such cases where the solid coke is periodically removed by oxidation in steam and air. Consequently, the metal surfaces, which are in contact with the carburizing process gas, must also have adequate oxidation resistance. In most applications this excludes Sn alloys and pure Cu and low alloyed Cu as useful alternative carburization-resistant materials. Even if the decoking step can be excluded in some processes, the start-up procedures after an inspection or other stops in operation which cause changes in temperature and pressure will be made easier by using an alloy having certain oxidation-resistance. Further, process variations in temperature and feedstock quality as well as the function of up-stream process equipment can lead to contamination of the process gases with e.g. sulfur, chlorine, alkali metallic compounds, water vapor and/or oxygen. A copper alloy, which is not protected by any oxide on the surface can thereby be affected by considerable corrosion and erosion. Likewise, chromium-containing copper alloys which are protected by chromium oxide, can also be damaged by the above-mentioned compounds, because the oxidation resistance of the chromium oxide is limited. Finally, copper has, and, in an even higher degree tin, high vapour pressures at temperatures over 500°C, which results in that, when these elements are present on the surface of the metal, vapor of said elements can be transported into the process system and leads to contamination of e.g. construction material, process fluids and catalysts as well as loss of thickness of the protective material.

There are techniques existing to coat construction material with thin layers of resistant or immune metals or coking-resistant metals such as Sn, Cu and are described in US-A-5,863,418 and EP-A-09003424 and WO 03014263 A1. Such thin layers, approximately <200µm thick, will be consumed by metal loss due to erosion and evaporation, as well as by reaction with the construction material, resulting in inadequate service lives at temperatures above approximately 500°C. Periodically re-coating of the surfaces exposed to corrosive gases requires either dismantling the process equipment and cleaning the surfaces to be coated and finally coating them or cleaning and re-coating them within the process equipment. The first method requires long shut-down periods, the

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second expensive re-designing and the development of as of today non-existing methods for in-situ cleaning and coating as well as for checking the integrity of the produced films. Therefore, periodic re-coating of thin coats will not be technologically and commercially practicable.

5

The alternative method to construct solid Cu-base members referred to in "THE ALUMINIUM BRONZES", MACKEN, PJ, SMITH, AA , COPPER DEVELOPMENT ASSN., 55 SOUTH ARDLEY STREET, LONDON W. 1, SECOND PUBLICATION 1966, CDA PUB. NO. 31, 263 PP ; 1966

10 is not an option above approximately 500°C for pressurised components or components that in some other way have to maintain structural integrity during their entire service life, due to the low mechanical strength of copper alloys above 400-500°C.

15 The use of such short lived solutions will therefore not remove the presently prevailing sense of uncertainty around operational concepts as predictability of maintenance costs and secondary damage risks related to outbreak of metal dusting attacks on process equipment.

20 The use of such short lived solutions is therefore not likely to support a broad industrial acceptance of new emerging and exergy efficient reforming design solutions, i.e. designs which are set to lower investment and operational costs of petrochemical and chemical plants and increase environmental sustainability, by reducing the requirement of hydrocarbon feedstock, and concomitantly
25 reducing green house gas emissions.

Particularly such solutions which feature thin coatings on load-carrying components or construction materials suffer from being short lived, and differ substantially from this solution in this specific respect.

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SUMMARY OF THE INVENTION

It is therefore an object of the present invention to provide a copper-base alloy according to claim 1 for use in CO-containing atmospheres, and/or hydrocarbon
5 containing atmospheres or solid carbon containing processes, such as gasification of solid carbonaceous materials, thermal decomposition of hydrocarbons and catalytic reforming, particularly, catalytic reforming under low-sulfur, and low-sulfur and low-water conditions.

10 It is another object of the invention to provide a product resistant or immune to oxidation, especially resistant in CO-containing atmospheres, and/or hydrocarbon containing atmospheres or solid carbon containing processes, i.e. processes such as gasification of solid carbonaceous materials, thermal decomposition of hydrocarbons and catalytic reforming, particularly, catalytic
15 reforming under low-sulfur, and low-sulfur and low-water conditions.

It is another object of the invention to provide a product resistant or immune to oxidation, especially resistant in CO-containing atmospheres, and/or hydrocarbon containing atmospheres or solid carbon containing processes, i.e.
20 processes such as gasification of solid carbonaceous materials, thermal decomposition of hydrocarbons and catalytic reforming, particularly, catalytic reforming under low-sulfur, and low-sulfur and low-water conditions at temperatures between 400 and 900°C and at pressures below 100 bar.

25 It is another object of the invention to provide a product that has a surface without the ability to catalytically activate the formation of solid coke.

It is a further object of the invention to provide a product which is resistant or immune to carburization, metal dusting and coking for use in CO-containing
30 atmospheres, and/or hydrocarbon containing atmospheres or solid carbon containing processes such as gasification of solid carbonaceous materials,

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thermal decomposition of hydrocarbons and catalytic reforming, particularly catalytic reforming under low-sulfur, and low-sulfur and low-water conditions.

5 It is a further object of the invention to provide a product which is resistant or immune to carburization, metal dusting and coking for use in CO-containing atmospheres, and/or hydrocarbon containing atmospheres or solid carbon containing processes such as gasification of solid carbonaceous materials, thermal decomposition of hydrocarbons and catalytic reforming, particularly catalytic reforming under low-sulfur, and low-sulfur and low-water conditions at
10 temperatures between 400 and 900°C and at pressures below 100 bar.

It is another object of the invention to provide a product resistant to loss of material by erosion or abrasion due to high gas velocities and suspended particles within the process gas stream.

15

Another object of the invention is to provide a product in which a Cu-base alloy which is resistant or immune to carburization, metal dusting and coking can be used at temperatures where copper-base alloys themselves have too low mechanical strength.

20

Another object of the invention is to provide a copper-base alloy as one component in a composite material in a minimum thickness of the corrosion resistant component of at least 0.5 mm for use at temperatures of 450-650°C in said composite form and in a minimum thickness of the corrosion resistant
25 component of at least 1.0 mm for use at temperatures above 650°C in said composite form.

25

It is a further object of the invention to provide a load bearing structural member, and specifically to render the thus manufactured products a long
30 service life in commercial applications.

30

It is another object of the invention to provide a product resistant to loss of material by copper evaporation.

BRIEF DESCRIPTION OF THE FIGURES

5

Fig. 1 shows the theoretical diffusion profile for Cu and Al after 4 years exposure at 750°C of a Cu-8%Al film with an initial thickness of 200µm.

10

Fig. 2 shows diagrammatically the weight loss of some comparative samples and one example of the present invention after exposure at 650°C over a period of time of 1000 hours (4 cycles to RT) in 25CO+3H₂O+H₂.

15

Fig. 3 shows the oxidation weight change during exposure to air at 850°C for seven different corrosion resistant Cu-Al base alloys.

20

Fig. 4 shows the partial pressure of CO molecules with different isotope composition in a furnace kept at 650°C containing a piece of alloy Q.

Fig. 5 shows the partial pressure of CO molecules with different isotope composition in an empty furnace kept at 650°C.

25

Fig. 6 shows a section in an phase diagram Cu-Ni-Al calculated with Thermo-calc for a given Al-content of 8 weight-%, where 1 – liquid, 2 – AlNi, 3 – FCC, 4 – BCC.

Fig. 7 shows the solubility of carbon (g carbon/g alloy) in an alloy with 4 weight-% Al and a varying Cu-Ni-relation at 750°C.

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DETAILED DESCRIPTION OF THE INVENTION

These objects will be fulfilled with a product composed of at least two different alloys as described in the following. The different alloys have to fulfil different

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requirements: the first is a load-bearing member, which provides the mechanical stability necessary for the temperature and pressure required by the process. The surfaces exposed to metal dusting, carburising and coking environments are covered with sufficiently thick layers of the corrosion resistant member. The corrosion resistant member is formed by a Cu-Al base alloy with the following composition (in weight-%):

Al: 2-20 weight-%, preferably 4-9 weight-%

The alloy may contain additional elements in order to optimise oxidation resistance or fabricability:

Si: 0-6 weight-%. In alloys with less than 9 weight-% Al preferably 1-3 weight-%. Sum of Fe, Ni, Co, Mn: 0-20 weight-%. For optimum resistance to metal dusting, the sum of Fe+Ni+Co+Mn should be less than 6.0 weight-% and the amount of any individual element should be less than 4.0 weight-%. Most preferably, the sum of Fe+Ni+Co+Mn should be less than 1.0 weight-%.

A more detailed description of the effect of different alloying additions follows below, in the section relating specifically to the corrosion-resistant Cu-Al base alloy.

In order to give structural integrity to the entire product and to ensure sufficient heat conducting ability across the wall of the product the different members have to be joined with a metallurgical bond along the entire contact surface. The necessary thickness of the corrosion resistant member is determined by the loss of material by evaporation, oxidation erosion and by diffusion into the load bearing component and the diffusion of element from the load bearing component into the corrosion resistant alloy. The diffusion process, which is illustrated in Fig. 1 leads to a successive deterioration of the corrosion resisting properties of the product if the thickness of the corrosion resistant alloy is too low. Therefore, if the product is intended for use over longer periods of time at temperatures over approximately 700°C, the thickness of the corrosion resistant alloy must be at least 1mm. In the presence of further deteriorating mechanisms, such as copper evaporation and erosion, the minimum thickness is 1mm even at temperatures in the range of 450-700°C. In the absence of

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these mechanisms, a thickness of 0.5 mm can be used at temperatures below 650°C.

Load-bearing member

- 5 The load-bearing member consists of an alloy with proven high temperature strength, such as for example UNS N08810, UNS N08811, UNS N06600, UNS N06601, UNS 34709 etc. It is required that the alloy used should have a sufficiently high mechanical strength at the operating conditions of the product in terms of temperature, pressure drop across the wall of the component, total
- 10 load of the product defined as the sum of the load from the weight of the load-bearing member and the weight of the corrosion-resistant Cu-base alloy. It is further required that an alloy is used that, in its as-delivered condition, fulfils relevant legal and standardisation requirements, e.g. pressure vessel approvals. Furthermore, if all surfaces of the load-bearing member are not
- 15 covered with a corrosion resistant alloy, it is required that the alloy itself should have sufficient corrosion resistance to the environment which it is exposed to.

Corrosion resistant member

- The surfaces of the product exposed to carburization, metal dusting and coking,
- 20 for use in CO-containing atmospheres, and/or hydrocarbon containing atmospheres or solid carbon containing processes such as gasification of solid carbonaceous materials, thermal decomposition of hydrocarbons and catalytic reforming, particularly catalytic reforming under low-sulfur, and low-sulfur and low-water conditions are covered by a Cu-Al alloy that may contain additional
- 25 elements to improve its properties. For use at temperatures of 450-650°C in a composite form as described in the present invention, the minimum thickness of the corrosion resistant component should be at least 0.5 mm. For use at temperatures over 650°C, the minimum thickness of the corrosion resistant component should be at least 1.0 mm.

30

Below, the effects of different alloying elements in the corrosion resistant alloy are described and specified.

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Aluminium

Aluminium is a necessary component in the alloy because of its capacity to form a protective alumina layer on the surface of the alloy in the temperature range of 300°C to 1300°C even in environments that solely contain trace amounts of oxygen. Aluminium can be added in amounts up approximately 9 weight-% without causing any major deterioration of the mechanical properties. It is estimated that this level is sufficient to achieve a necessary corrosion resistance in the majority of considered applications. If necessary, higher Al levels may be used, but in those cases, the ability of the alloy to be cold formed is limited. However, such levels may be used for example in hot-extruded sections such as circular tubes or in hot-rolled bar or plate. Aluminium should be added in an amount of up to 20 weight-%, preferably up to 13 weight-%, most preferably up to 9 weight-%, but not less than 2 weight-%, preferably not less than 4 weight-%.

15

Silicon

Silicon can be used in order to promote the protective effect of aluminium in this type of alloy by forming aluminosilicates, which have higher formation rates compared to that of pure alumina. In this type of alloy the lower starting temperature for the formation of a protective oxide is favourable. Therefore silicon can be added to the alloy in order to improve the oxide formation at low temperatures. If the Al content is below 9 weight-%, a content of silicon higher than 0.5 weight-% is positive for the oxidation resistance, but also an alloy which does not contain silicon forms a protective alumina scale and therefore the content of silicon should be up to 6 weight-%, preferably 1-3 weight-%.

25

Nickel, iron, cobalt, manganese

Transition metals, especially iron, nickel and cobalt are known to have a strong catalytic effect on the formation of coke. The protecting capacity of the alumina layer, which will be formed on the surface of the alloy, allows proportionately high levels of these elements, but not more than a total of 20 weight-% of iron, nickel and cobalt.

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Nickel, and, to a minor degree cobalt, can be used in order to

- increase the maximum temperature of use by increasing the melting point of the alloy up to approximately 1100°C and consequently
- allow the use of production methods that involve steps through temperatures
- 5 above the melting point of a binary Cu-Al alloy, which is approximately 1030-1080°C and
- improve the mechanical strength of the alloy at increased temperatures, from approximately 800°C to approximately 1100°C.

- 10 An increased content of nickel, cobalt, iron and/or manganese can lead to an improved tendency of carburization and to a decreased resistance to metal dusting and coking. Therefore, the content of these elements should be kept as low as possible while still allowing the use of effective production methods. A practical maximum above which the deterioration of the corrosion resistance is
- 15 expected to be prohibitive is 20 weight-%. The nickel in the alloy can completely or partly be replaced by iron and/or cobalt.

A pure Cu-Al-alloy according to the present invention has a melting point between 1030° and 1080°C, dependent on the content of Al.

- 20 If an optimum resistance to metal dusting and coking is desired, the content of each of the elements in the group Fe, Mn, Ni, Co should be less than 4.0 weight-% per element. The total content of these elements should in that case not exceed 6.0 weight-%, preferably not exceed 1.0 weight-%.

- 25 Iron can be used to improve the hot working characteristics of Cu-Al alloys, and it can therefore be added in amounts of up to 10 weight-%, preferably up to 5 weight-%, most preferably 0.5-4 weight-%.

30 **Reactive Additions**

In order to further increase the oxidation resistance at higher temperatures, it is common practice to add a certain amount of reactive elements, such as Rare

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Earth Metals (REM), e.g. yttrium, hafnium, zirconium, lanthanum and/or cerium. One or more of this group of elements should be added in an amount not exceeding 1.0 weight-% per element. The total content of those elements should not exceed 3.0 weight-%, preferably not exceed 0.5 weight-%, most preferably 0.01-0.2 weight-%.

Copper

The main component, which amounts the balance of the alloy of the present invention, is copper. Copper is known to be resistant or immune to catalytic activity and coking. Until today it has not been possible to use pure copper in these applications, due to its high oxidation rate when in contact with oxygen. The alloy comprises up to 98 weight-% Cu, but at least 60 weight-% Cu, preferably at least 74 weight-%, most preferably at least 80 weight-% Cu.

Further, the alloy comprises normally occurring alloying additions and impurities.

The product according to the present invention can be machined or manufactured by conventional metal working or metal forming processes, to a composite construction material in the shape of tubes, pipes, plates, strip and wire. It can also be produced by deposition of the corrosion resistant alloy onto the surface or surfaces of a semi-finished product of the load bearing alloy using known deposition techniques.

25

DESCRIPTION OF PREFERRED EMBODIEMENTS OF THE INVENTION

Examples 1-5 are related to the corrosion resisting properties of the Cu-base alloy, in particular its resistance to metal dusting, carburisation and coke formation and its ability to form a protective oxide with an excellent self-healing ability and the choice of composition of such an alloy.



Examples 6-9 are related to the detailed design of a finished product fulfilling certain requirements in terms of mechanical properties as well as corrosion resistance.

5 EXAMPLE 1

Static laboratory experiments were executed in a tube furnace in a strongly coking atmosphere. The metal dusting resistance of stainless steel of standard quality and the Cu-base alloys A to M of the present invention was measured and evaluated. Table 1 shows the chemical compositions of the investigated materials, Table 2 shows the compositions of the embodiments A to Q according to the present invention. All contents are given in weight-%.

Table 1

Example no.	C	Cr	Ni	Mo	N	Si	Mn	P	S	Ti	Ce
304L (bar)	0,013	18,35	10,15	0,39	0,043	0,42	1,26	0,024	0,004		
304L (plate)	0,015	18,20	10,10	0,39	0,043	0,43	1,42	0,021	0,001	-	-
Alloy 800HT	0,063	20,37	30,10	0,05	0,009	0,73	0,53	0,009	0,001	0,5	-
353MA	0,052	25,10	34,10	0,20	0,175	1,56	1,40	0,020	0,001	-	0,06

15 Table 2

	Al	Ni	Fe	Si	Mn	Cr	Co	Ce	Zr	La	Cu
A	8,0	0,02	0,02		0,005	0,002			0,0001		balance
B	5,6	<0,1	<0,1	1,7	<0,1	<0,1	<0,1			0,0014	balance
C	9,5	<0,1	<0,1	4,8	<0,1	<0,1	<0,1			0,0012	balance
D	8,4	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1			0,0004	balance
E	6,3	<0,1	<0,1	0,6	6,3	<0,1	<0,1			0,0007	balance
F	15,1	10,1	<0,1	<0,1	<0,1	<0,1	<0,1			0,0004	balance
G	2,8	<0,1	<0,1	0,1	<0,1	<0,1	<0,1			0,016	balance
H	6			2							balance
I	8			2	8						balance
J	10,7	7,0		<0,1	6,6					0,0018	balance
K	15	15									balance
L	12,2	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1			0,075	balance
M	4,9	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1	0,068		0,055	balance
N	9,6						5,0				balance
O	13,7						9,8				balance
P	10,5	<0,5	3,5	<0,1	<0,1	<0,1	<0,1				balance
Q	8,1	<0,1	<0,1	2,1	<0,1	<0,1	<0,1				balance

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The test samples were cut from plates or bars into a rectangular shape with dimensions of approximately $10 \times 12 \times 3$ mm and prepared by grinding with 600 mesh. Some of the test samples were surface treated by a standard pickling operation in 1.8M HNO_3 + 1.6M HF at 50°C during 8-40 min. or treated by an electro polishing operation (50g CrO_3 + 450ml orthophosphoric acid, 20V). The samples were cleaned in acetone prior to testing and placed in the cold furnace. In order to reach a low oxygen partial pressure, pure hydrogen was flushed through the furnace for three hours before introducing the reaction gas and heating to temperature. The gas flow rate was 250 ml/min, which corresponds to a gas velocity over the specimen of 9 mm/s. The temperature was stabilized at 650°C after 20 minutes heating. The input composition of the reaction gas was 25% CO +3% H_2O +72% H_2 . The laboratory exposure was conducted at $650^\circ\text{C}/1000\text{h}$ in a quartz tube furnace with a diameter of 25mm. Four temperature cycles down to $100\text{-}200^\circ\text{C}$ and back to 650°C , each with a duration time of about 4-5h, were conducted in order to raise the carbon activity and promote initiation of metal dusting.

The results are presented as weight loss measurements after cleaning the samples from coke and graphite as presented in Figure 2, where:

20 Table 3

Comparative Example no.	Alloy	Product condition	Surface modification
1	304L	bar	Annealed
2	304L	bar	electro-polished
3	304L	bar	Ground
4	304L	bar	Pickled
5	304L	plate	Annealed
6	304L	cold rolled plate	Ground
7	304L	cold rolled plate	electro-polished
8	800 HT	plate	Ground
9	800 HT	plate	Pickled
10	353 MA	plate	overpickled
11	Alloy A	plate	untreated

As shown in Figure 1, all comparative steels (Examples 1-10) suffered from metal dusting with formation of pits and coke during the 1000 h exposure as function of the measurable weight gain. However, the alloy of the present invention (Example 11) was practically non-reactive in this atmosphere with no weight change or coke formation. Example 11 has been exposed for totally 4000/hours in similar atmospheres (4x1000h at 650°C) with any measurable or visible changes.

EXAMPLE 2

The alloys according to the examples B to O with compositions according to Table 2 were produced by melting in a protective gas atmosphere of argon, followed by casting.

These alloys can, when exposed to oxidizing atmosphere in the temperature range of 300° to 1050°C, form a protective alumina or mixed aluminum containing oxide, which restrains further oxidation of the alloy and restrains evaporation of copper from the alloy, which makes the alloy more resistant to material loss by copper evaporation. This is illustrated in Table 4 which shows the average weight change per hour ($\text{g}/(\text{m}^2\text{h})$) after cyclic oxidation in air during between 48h and 454h for 7 different Cu base alloys and which makes visible that there is little difference between the different alloys at 400°C and 550°C. Alloy D is clearly inferior to the other alloys at higher temperatures with respect to oxidation. The oxide formed on alloy E is prone to spalling during cooling from 850°C. The superior oxidation resistance at 850°C of alloys B, L and N at 850°C is illustrated in Figure 3. The results indicate that optimum oxidation resistance is achieved in alloys containing at least 9 weight-% Al or a combination of Al and Si such that $\text{Al} + 2 \cdot \text{Si}$ (in weight-%) is greater than or equal to 9. In the latter case alloy B shows that a Si-content of 1.7 weight-% is sufficient to give adequate oxidation resistance to an alloy with 5.6 weight-% Al. A Co-content of 5 weight-% does not result in any deterioration of the oxidation resistance, but with a Co-content of 10 weight-% a minor deterioration of the oxidation resistance is evident. Likewise, 6.3 weight-% Mn causes the alloy to become sensitive to oxide spalling. It can be expected that iron and nickel have

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similar effects as manganese and cobalt with respect to the oxidation resistance. It can thus be concluded that for optimum oxidation resistance an alloy composition of 5-12 weight-%Al, 1-3 weight-%Si and less than 6 weight-% of Fe+Mn+Ni+Co is desirable.

5

Table 4

	B	D	E	L	N	O	P
400°C	0,0024	0,0015	0,0049	0,0024	0,0048	0,0023	0,0016
550°C	0,0022	0,0013	0,0031	0,00095	0,0015	0,00094	0,0041
700°C	0,014	0,052	0,010	0,0073	0,015	0,017	0,012
850°C	0,030	0,58	-0,038	0,022	0,0048	0,062	0,054

EXAMPLE 3

- 10 The alloy according to example Q with composition according to Table 2 was produced by melting in a protective gas atmosphere of argon, followed by casting. The alloy was exposed to 23 mbar CO-gas at 600°C for 465h. The CO-gas was initially composed of a mixture of CO-molecules composed of ^{13}C and ^{18}O isotopes and CO molecules composed of ^{12}C and ^{16}O isotopes, By
- 15 measuring the rate of transformation of $^{13}\text{C}^{18}\text{O}$ and $^{12}\text{C}^{16}\text{O}$ to $^{13}\text{C}^{16}\text{O}$ and $^{12}\text{C}^{18}\text{O}$ the catalytic activity of alloy Q with respect to breakdown and recombination of CO can be determined. The breakdown reaction is considered to be important as a first step in any metal dusting, carburisation or coking process.
- 20 The transformation of $^{13}\text{C}^{18}\text{O}$ and $^{12}\text{C}^{16}\text{O}$ in the presence of alloy Q is shown in Figure 4 measured by mass spectrometry. As a comparison, Figure 5 shows the transformation of the same gases in an empty furnace. The furnace material is silica. There is no significant difference in the catalytic activity between Alloy Q and the empty silica furnace. The latter in turn can be considered as an inert material, i.e. alloy Q completely lacks any catalytic activity with respect to CO,
- 25 and can thus be considered as a highly resistant or immune material with respect to metal dusting, carburisation and coking in CO containing gases.

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EXAMPLE 4

A laboratory exposure was performed in a tube furnace in a highly carburizing atmosphere. The relative tendency to coke formation at 1000°C was evaluated
5 between a standard grade stainless steel and several Cu-base alloys with compositions according to tables 1 and 2.

The test samples were cut from cast material into rectangular shape with dimensions of approximately 10×15× 3 mm and prepared by grinding to 600
10 mesh. The samples were cleaned in acetone prior to testing and placed in the cold furnace. To reach a low oxygen partial pressure, pure hydrogen was flushed through the furnace for three hours before introducing the reaction gas and heating to temperature. The gas flow rate was 250 ml/min, which corresponds to a gas velocity over the specimen of 9 mm/s. The temperature
15 stabilizes at 1000°C after 30 minutes heating. The reaction gas had an input composition of 83%CO+17%H₂. The laboratory exposure was conducted at 1000°C/100h in a quartz tube furnace with a diameter of 25 mm.

The results from the coking tests are presented in Table 5 as weight gain due to coke/graphite formation on the sample surface.

20

Table 5

Material	Coke formation at 1000°C [mg/cm ² /100h]
Alloy 800HT	5.2
P	1.0
Q	0
L	0
N	0.5

It is evident that even relatively small amounts of Co, Ni and Fe are detrimental
25 to the coking resistance of the Cu base alloy. Therefore, it is clear that the total amount of Fe+Ni+Co+Mn should be below 3 weight-% in order to obtain

optimum properties. However, even with a total content of Fe+Ni+Co+Mn of up to 6 weight-%, the alloy is superior to the standard material Alloy 800HT.

EXAMPLE 5

5 Fig. 6 shows a section of a phase diagram Cu-Ni-Al calculated with Thermo-calc for a given Al-content of 8 weight-%. Graph 1 shows the solidus/liquidus temperature, graph 2 shows the area of stability for the phase NiAl, graph 3 shows the area of stability for the cubic close-packed solid solution of copper and nickel, which also can contain minor contents of e.g. aluminium. Graph 4
10 shows the area of stability for the phase, which in the pure Cu-Al-system is called β .

Fig. 6 and Table 6 show the effect of different contents of copper, nickel and aluminium in an alloy of 92 weight-% (Cu+Ni) and 8 weight-% Al at the solidus- and liquidus temperatures. The Figure 6 shows that only by increasing the
15 content of nickel above 20 weight-% its melting point can be brought to exceed 1100°C.

Fig. 7 and Table 6 show the effect of the Ni, Cu and Al contents on the solidus temperature and carbon solubility in an Cu-Al-Ni alloy. The diagram shows, that
20 for nickel contents above approximately 10 weight-% the solubility of carbon is strongly increased with increasing nickel content. The rate of carburization of an alloy is to a high extent determined by the solubility of carbon in the alloy and also the phenomena of metal dusting and coking are expected to increase with increasing carbon solubility. Therefore, it is desirable that the solubility of carbon in the alloy is as low as possible, and a consequence of this is that the
25 nickel content should be lower than 10 weight-% in order to obtain an optimum resistance to carburization, coking and metal dusting, preferably lower than 1 weight-%.

The reason for such low level of the Ni-content is required in order to obtain optimum properties is, that nickel, besides affecting the solubility of carbon also
30 catalyzes coking, which is unfavorable.

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Table 6

Example	Ni weight-%	Al weight-%	Cu weight-%	Solidus temperature °C	Carbon solubility at 750°C g carbon/g alloy
R	0	4	96	1070	2,50E-13
S	2	4	92	1080	3,30E-13
T	5	4	91	1090	3,50E-13
U	10	4	86	1100	6,60E-13
V	20	4	76	1130	5,00E-12
W	0	8	92	1040	9,65E-13
X	2	8	90	1030	8,22E-13
Y	5	8	87	1040	5,40E-13
Z	10	8	82	1070	3,00E-13
AA	20	8	72	1100	8,00E-13
Comp. Example 1	60	4	36	1270	1,90E-07
Comp. Example 2	60	8	32	1200	7,00E-08
Comp. Example 3	30	4	66	1160	7,00E-11
Comp. Example 4	40	4	56	1190	1,20E-09
Comp. Example 5	50	4	46	1230	1,90E-08
Comp. Example 6	30	8	62	1130	7,00E-12
Comp. Example 7	40	8	52	1150	1,00E-10
Comp. Example 8	50	8	42	1180	2,40E-09

EXAMPLE 6

- 5 The person skilled in the art realizes that for the product according to the present invention it is necessary to be designed with a load carrier at elevated temperatures, i.e. temperatures above approximately 400°C. With this purpose a Cu base alloy can be machined to a component in a composite or bimetallic composite solution, which will be used as construction material in the different shapes as mentioned above. The latter is especially valid if the alloy has low contents of iron and nickel.
- 10

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The product is in the shape of tubes or plate or strip or wire, where the inner load-carrying layer is coated at one or both surfaces with the Cu base alloy specified in previous examples. Some of the methods, which can be used in order to produce a composite solution of the alloy and a load carrier are co-extrusion, co-welding or co-drawing and shrinkage of one tube on the load carrying component and one outer and/or inner tube of the alloy according to the invention, possibly followed by a heat treatment in order to obtain a metallurgical binding between the components. A similar method for the production of plate or strip is to hot- or cold-roll together two or more plates or strips. Composite plates or -tubes can also be produced by explosion welding of two or more different plates or tubes of a load carrier and the alloy according to the invention. An outer- and/or inner-component can also be applied on a load carrier by help of a powder metallurgical technique, such as HIP (Hot Isostatic Pressing) or CIP (Cold Isostatic Pressing). In these cases the load carrier could be in the shape of tubes, pipes, plate, strip or wire or other suitable product form. After pressing, the formed composite will be further machined by e.g. hot extrusion and/or welding, drawing and forging.

Other methods for the production for the production of composite material are electrolytic coating of copper and aluminium on the load carrying component, possibly followed by an annealing in order to homogenize the coating or a gas phase deposition of copper and aluminium by e.g. vaporization, pack cementation, sputtering, chemical vapor deposition (CVD) or other methods. Aluminium and copper can also be deposited on the load carrier e.g. by dipping in a melt or by overlay welding. These methods are possible to use in order to produce all of the above-mentioned product forms. Different coating methods can be used in order to supply copper and aluminium to the alloy. In such cases, a final heat-treatment is required in order to homogenize the alloy with the purpose to keep its corrosion properties.

Composite strip or composite plates, produced according to the above description can be welded together to longitudinal welded or helical welded composite tubes with the Cu base alloy on the inner and/or outside of the tube.

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Suitable load carriers in the above mentioned product forms are such high temperature alloys, which today are used for their mechanical strength and oxidation resistance in the actual temperature range, but which have insufficient metal dusting, carburisation, coking or nitridation resistance for use in the environments to which the present invention relates. This includes for temperatures lower than 700°C martensitic or bainitic or ferritic iron alloys with additions of e.g. chromium, molybdenum, vanadium, niobium, tungsten, carbon and/or nitrogen in order to obtain mechanical strength at high temperature. At temperatures above approximately 500°C it is in many cases common practice to use austenitic iron-chromium-nickel alloys, which are possibly mechanically strengthened as load carrier by alloying with e.g. molybdenum, vanadium, niobium, tungsten, carbon and/or nitrogen. In both of those groups of alloys chromium and sometimes aluminium and/or silicon is used in order to give the load carrier an improved corrosion resistance. In those cases, where the product according to the invention is composed of such a load carrier covered on both surfaces with the corrosion resistant Cu base alloy of, the Cu base alloy according to the invention will deliver the corrosion resistance that is required. By that means, alloys whose maximum temperature of use in other applications is limited by the corrosion resistance are being able to be used as load carriers at higher temperatures than otherwise. In those cases, where product according to the invention is only covered at one surface of the load carrier by the corrosion resistant Cu base alloy, it is necessary that the load carrier itself has a sufficient corrosion resistance in the environment its free surface is exposed to.

25

EXAMPLE 7

As an example of how a tubular product for use in metal dusting conditions is designed to meet the different requirements on such a product a description of a finished tubular product follows.

30

The tube for use in applications where a corrosive gas exchanges heat with itself across the tube wall consists of a load bearing component of Alloy 800HT

(UNS N08811) with a protective layer of a Cu-base alloy of composition Cu-8.5 weight-%Al-1.0 weight-%Si-0.5 weight-%Fe on both inner and outer surfaces. One example of such a tube has a diameter of 60.3 mm and a total thickness of 3.91 mm. In this finished product, the outer corrosion resistant layer has a thickness of 1.0mm, and the inner corrosion resistant layer a thickness of 0.7mm, whereas the load bearing component has a thickness of 2.2 mm. At 900°C, this means, that the maximum allowable pressure drop according to the ASME boiler and pressure vessel code, section VIII, division I, is approximately 5.5 bar. Since the gas exchanges heat with itself, the pressure drop across the tube wall is expected to be less than 5 bar, even in processes that operate at absolute pressures in the range 10-100 bar. Thus, the product described in the previous section fulfils the necessary requirements to be used at as high temperatures as 900°C.

It should be clear to the person skilled in the art that the tubular product with the corrosion resistant alloy covering only the inner or only the outer surface are also possible with a wide range of dimensions and compositions of the Cu base alloy and the load bearing alloy.

EXAMPLE 8

An example of this is a tube which conducts a gas with a carbon activity greater than unity at a temperature range of 450-700°C in its interior and on its outer surface is cooled by air with temperature in the range 200-700°C. For this reason such a tube is covered with a metal dusting resistant Cu-base alloy on its inner surface, but the outer surface must still have a sufficient oxidation resistance with respect to the hot air. Using a proven alloy such as Alloy 600 (UNS N 08600) with 6 mm wall thickness and 2 mm thick Cu-7Al-0.2Si-0.5 weight-%Ni alloy on the inner surface allows at least 10 years service life with an internal pressure of 10 bar.

EXAMPLE 9

A further example of is a tube which conducts steam in its interior and which is heated from the outside by a gas with a carbon activity greater than unity at a temperature range of 200-600°C. In this case, the outer surface is exposed to the metal dusting conditions, whereas the inner surface is not exposed to any carbon related corrosion. For this reason such a tube is covered with a metal dusting resistant Cu-base alloy on its outer surface, and an alloy with sufficient steam corrosion resistance and mechanical strength is used as the load bearing member. One alloy that fulfils these demands is Alloy 800HT (UNS N 08811).

With a tube of outer diameter 50 mm and a wall thickness of 3.7 mm, using a 0.9mm thick Cu-5.8 weight-%Al-1.0 weight-%Si layer on the outer tube surface. In that case the Alloy 800HT thickness is 2.8 mm which means that the maximum internal steam pressure that can be allowed is 100 bar.

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Claims

1. Use of a copper-base alloy containing (in weight-%):
- | | |
|----|--------|
| Al | 2 - 20 |
| Si | ≥0 - 6 |
- 5 One or more of the group of Rare Earth Metals (REM),
such as yttrium, hafnium, zirconium, lanthanum and /or cerium
up to 1.0 of each element
in total up to 3.0
- One or more of the elements iron, nickel, cobalt and maganese,
10 in total up to 20
- Cu balance
and normally occurring alloying additions and impurities.
- In CO-containing atmospheres, and/or hydrocarbon containing atmospheres
or solid carbon containing processes, such as gasification of solid
15 carbonaceous materials, thermal decomposition of hydrocarbons and
catalytic reforming, particularly, catalytic reforming under low-sulfur, and
low-sulfur and low-water conditions.
- 20 2. Use of a copper-base alloy according to claim1 in CO-containing
atmospheres, and/or hydrocarbon containing atmospheres or solid carbon
containing processes, i.e. processes such as gasification of solid carbonaceous
materials, thermal decomposition of hydrocarbons and catalytic reforming,
particularly, catalytic reforming under low-sulfur, and low-sulfur and low-water
25 conditions at temperatures between 400 and 900°C and at pressures below 100
bar.
3. Use of a copper-base alloy according to claims 1 and 2 as one
component in a composite material in the shape of tubes, pipes, plate, strip and
30 wire in CO-containing atmospheres, and/or hydrocarbon containing
atmospheres or solid carbon containing processes, for example, gasification of
solid carbonaceous materials, thermal decomposition of hydrocarbons and
catalytic reforming, particularly, catalytic reforming under low-sulfur, and low-
sulfur and low-water conditions.

4. Use of a copper-base alloy according to claim 1 to 3 as one component in a composite material.
- 5 5. Use of a copper-base alloy according to claim 1 to 4, where the copper-base alloy is provided in a minimum thickness of the corrosion resistant component of at least 0.5 mm for use at temperatures of 450-650°C in said composite form.
- 10 6. Use of a copper-base alloy according to claim 1 to 4, where the copper-base alloy is provided in a minimum thickness of the corrosion resistant component of at least 1.0 mm for use at temperatures above 650°C in said composite form.
- 15 7. Use of a copper-base alloy according to claim 1 to 6 as construction material in the shape of tubes, pipes, plate, strip and wire.
8. Copper-base alloy according to claims 1 to 7 , c h a r a c t e r i z e d in that said alloy is resistant or immune to carburization, metal dusting and coking and resistant to oxidation and has the following composition (all contents in weight-%):
20

Al	2 - 20
Si	≥0 - 6
One or more of the group of Rare Earth Metals (REM), such as yttrium, hafnium, zirconium, lanthanum and/or cerium up to 1.0 weight-% of each element in total up to 3.0	
One or more of the elements iron, nickel, cobalt and maganese, In total up to 20 weight-%	
Cu	balance

30 and normally occurring alloying additions and impurities.

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9. Copper-base alloy according to claim 8, **characterized** in that said alloy comprises up to 20 weight-% Al, preferably 4-13 weight-% Al, most preferably 4-9 weight-% Al and the balance Cu and normally occurring alloying additions and impurities.

5

10. Copper-base alloy according to claim 8, **characterized** in that said alloy comprises up to 6 weight-% Si, preferably up to 5 weight-% Si and the balance Cu and normally occurring alloying additions and impurities.

10

11. Copper-base alloy according to claim 8, **characterized** in that said alloy comprises one or more of the group of Rare Earth Metal (REM), Yttrium, Hafnium, Zirconium, Lanthanum and/or Cerium in a content up to 1.0 weight-% each.

15

12. Copper-base alloy according to claim 8, **characterized** in that said alloy comprises one or more of the group of Rare Earth Metal (REM), Yttrium, Hafnium, Zirconium, Lanthanum and/or Cerium in a total content content up to 3.0 weight-%, preferably 0.5 weight-%, most preferably 0.01-0.2 weight-%.

20

13. Copper-base alloy according to claims 7 to 12, **characterized** in that said alloy is resistant to oxidation in CO-containing atmospheres, and/or hydrocarbon containing atmospheres or solid carbon containing processes, for example, gasification of solid carbonaceous materials, thermal decomposition of hydrocarbons and catalytic reforming, particularly, catalytic reforming under low-sulfur, and low-sulfur and low-water conditions at temperatures between 400 and 900°C and at pressures below 100 bar.

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ABSTRACT

Use of a copper-base alloy, which is resistant or immune to carburization, metal dusting and coking, resistant to oxidation and said alloy having the following composition (all contents in weight-%):

5 Al 2 - 20

Si ≥0 - 6

One or more of the group of Rare Earth Metals (REM),
such as yttrium, hafnium, zirconium, lanthanum and/or cerium

up to 1.0 of each element

10 in total up to 3.0

One or more of the elements iron, nickel, cobalt and manganese,
in total up to 20

Cu balance

and normally occurring alloying additions and impurities

15

as construction components in CO-containing atmospheres, and/or
hydrocarbon containing atmospheres or solid carbon containing processes, for
example, gasification of solid carbonaceous materials, thermal decomposition of
hydrocarbons and catalytic reforming, particularly, catalytic reforming under low-
20 sulfur, and low-sulfur and low-water conditions at temperatures between 400
and 900°C and at pressures below 100 bar and which is resistant to loss of
material by copper vaporization.

Figure 1

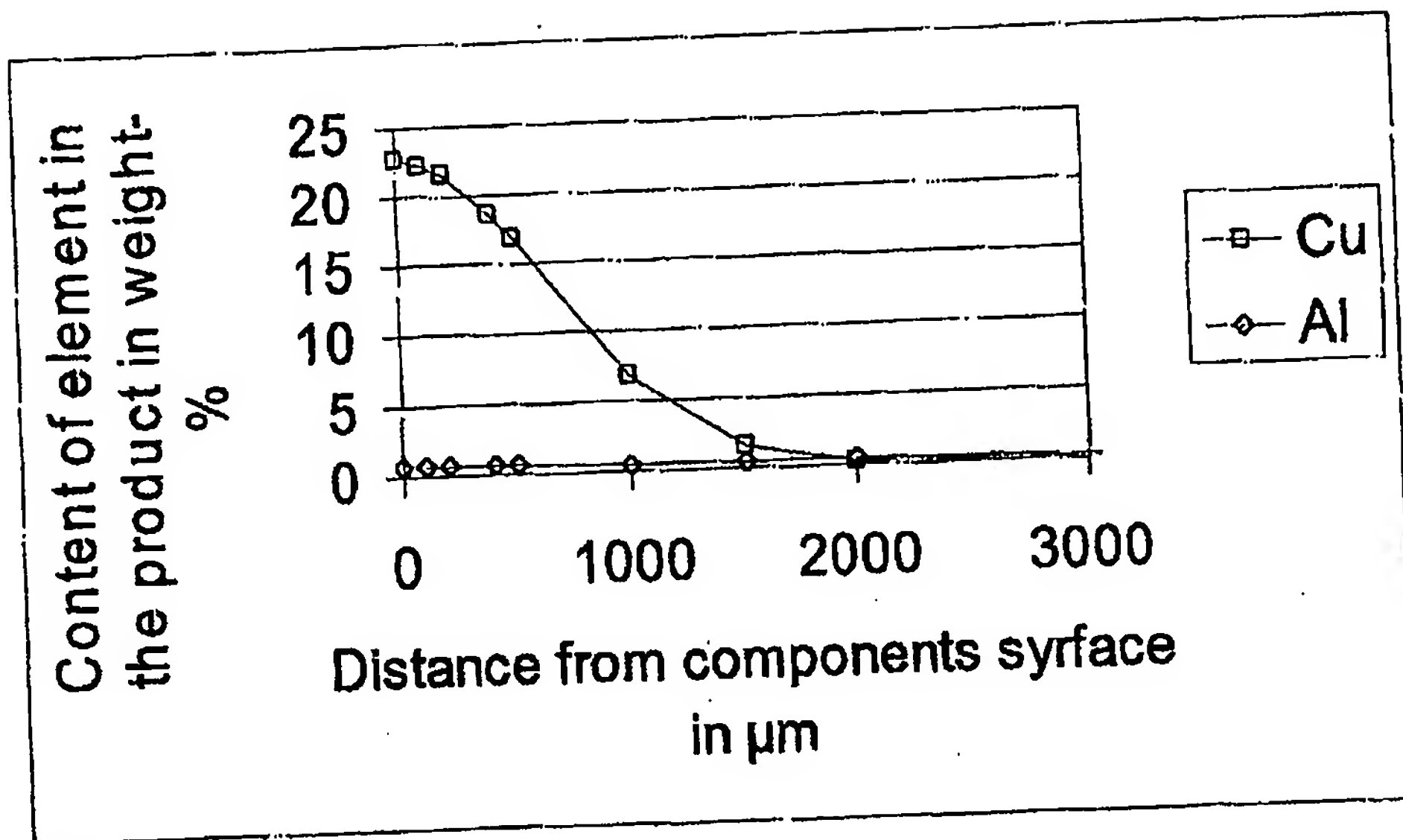
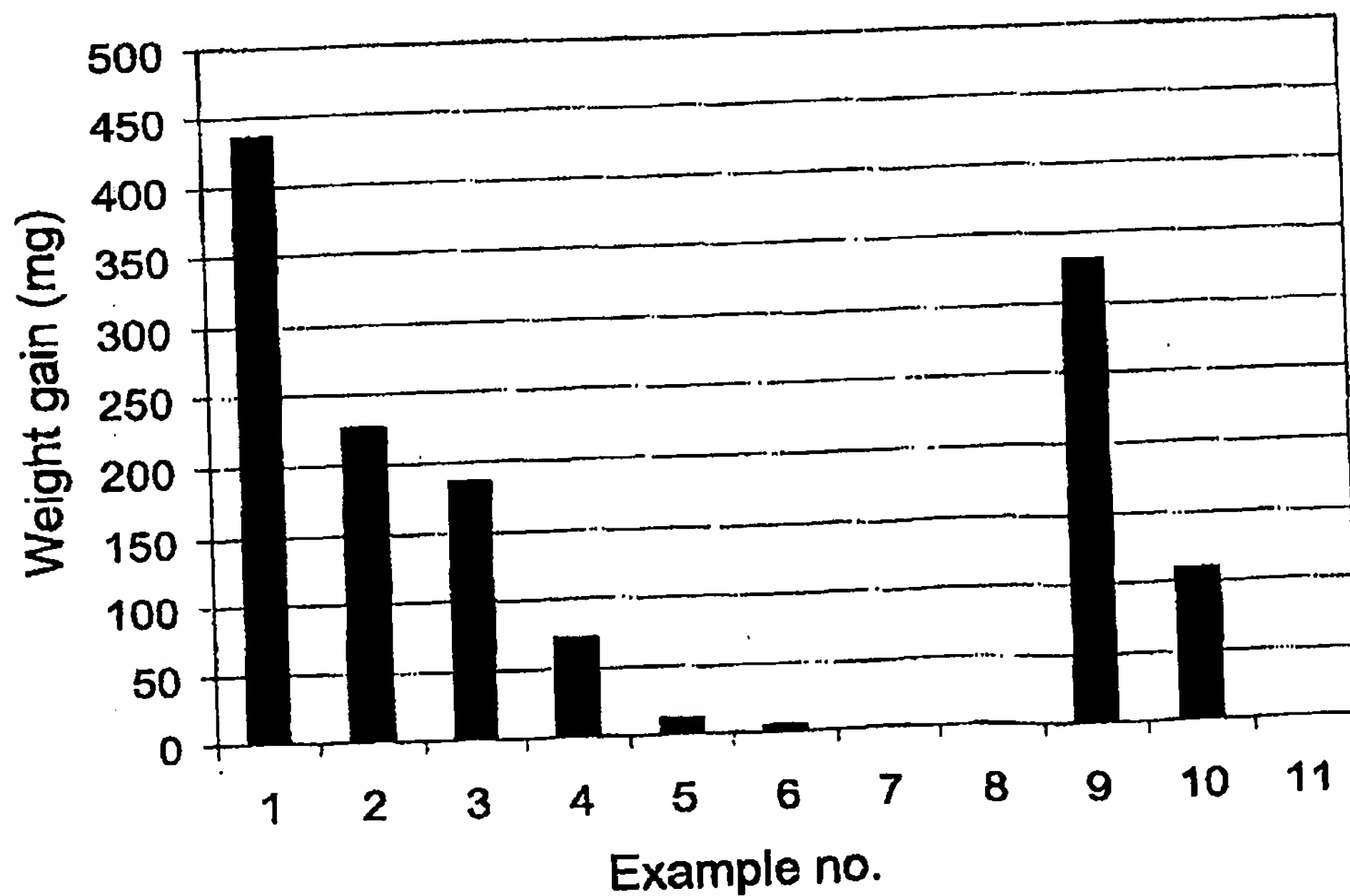


Figure 2



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Figure 3

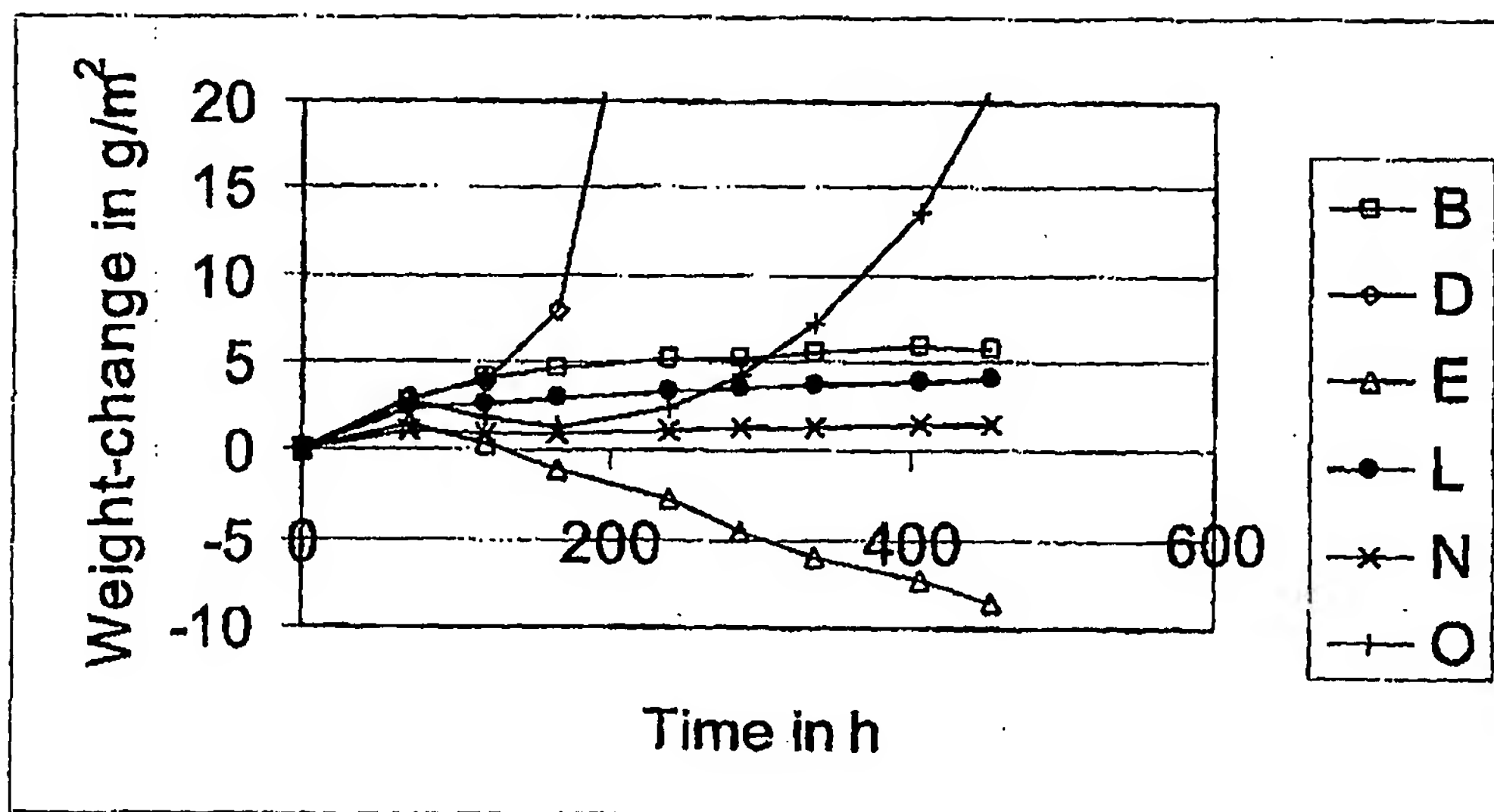
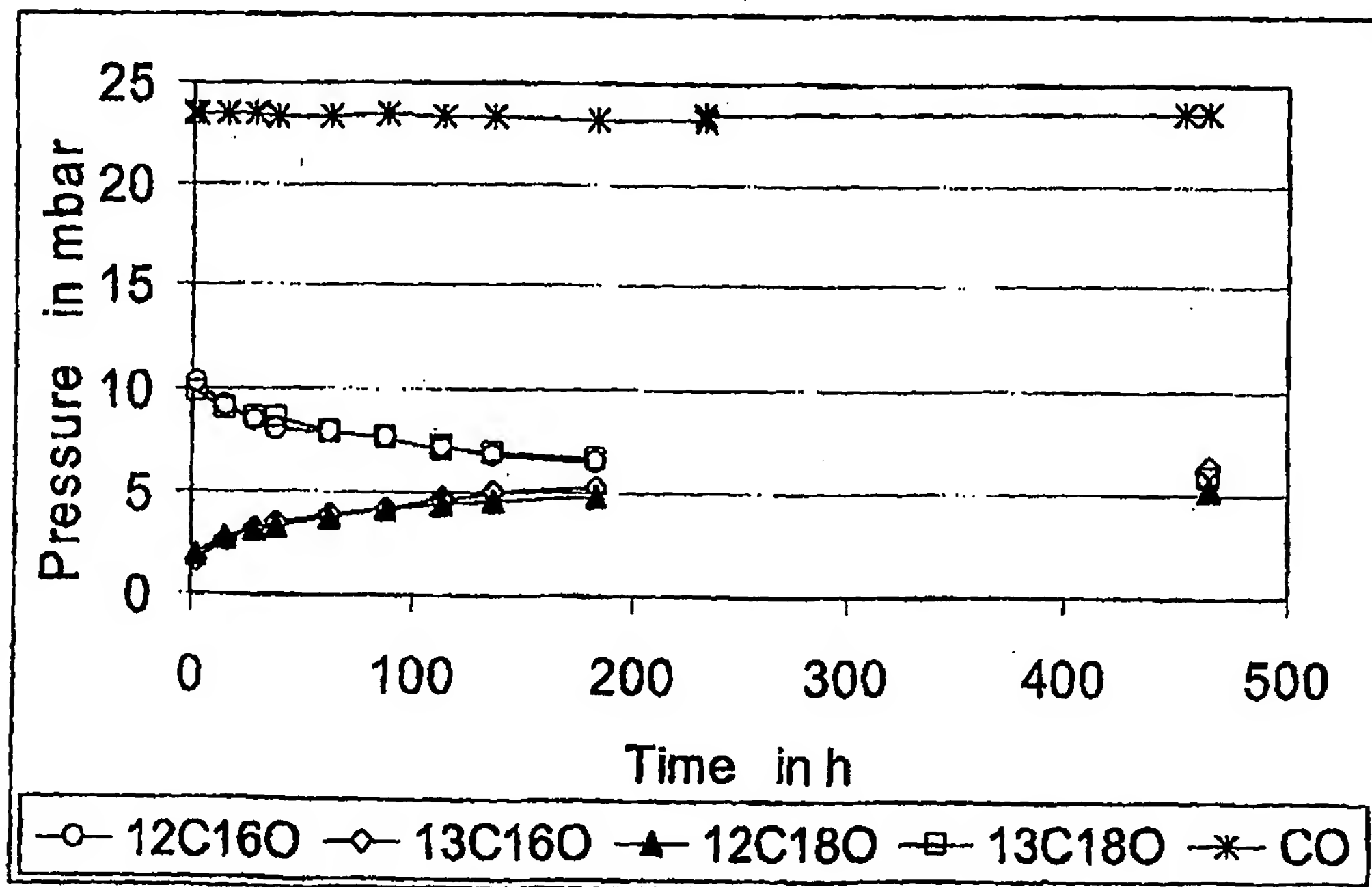


Figure 4



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Figure 5

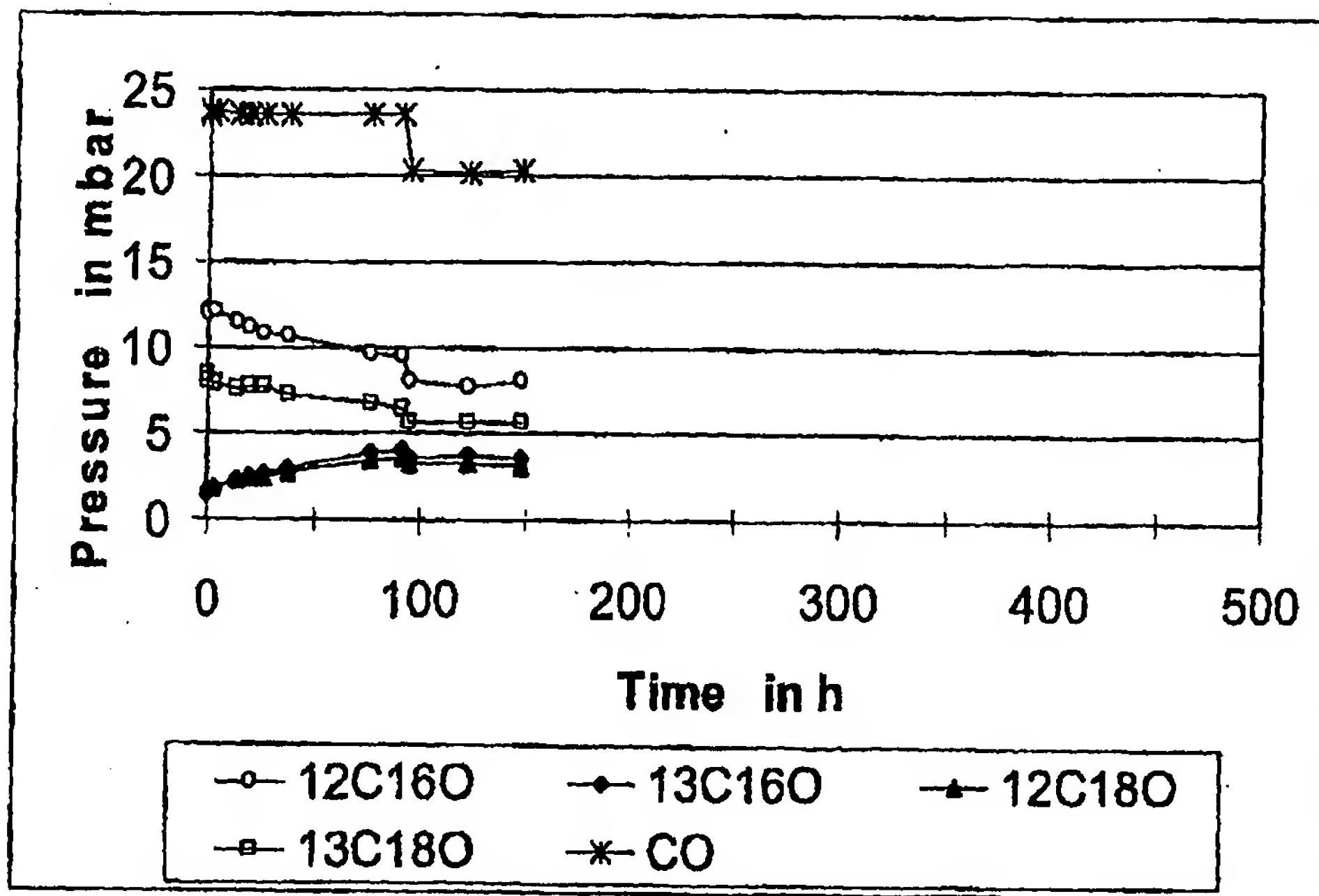
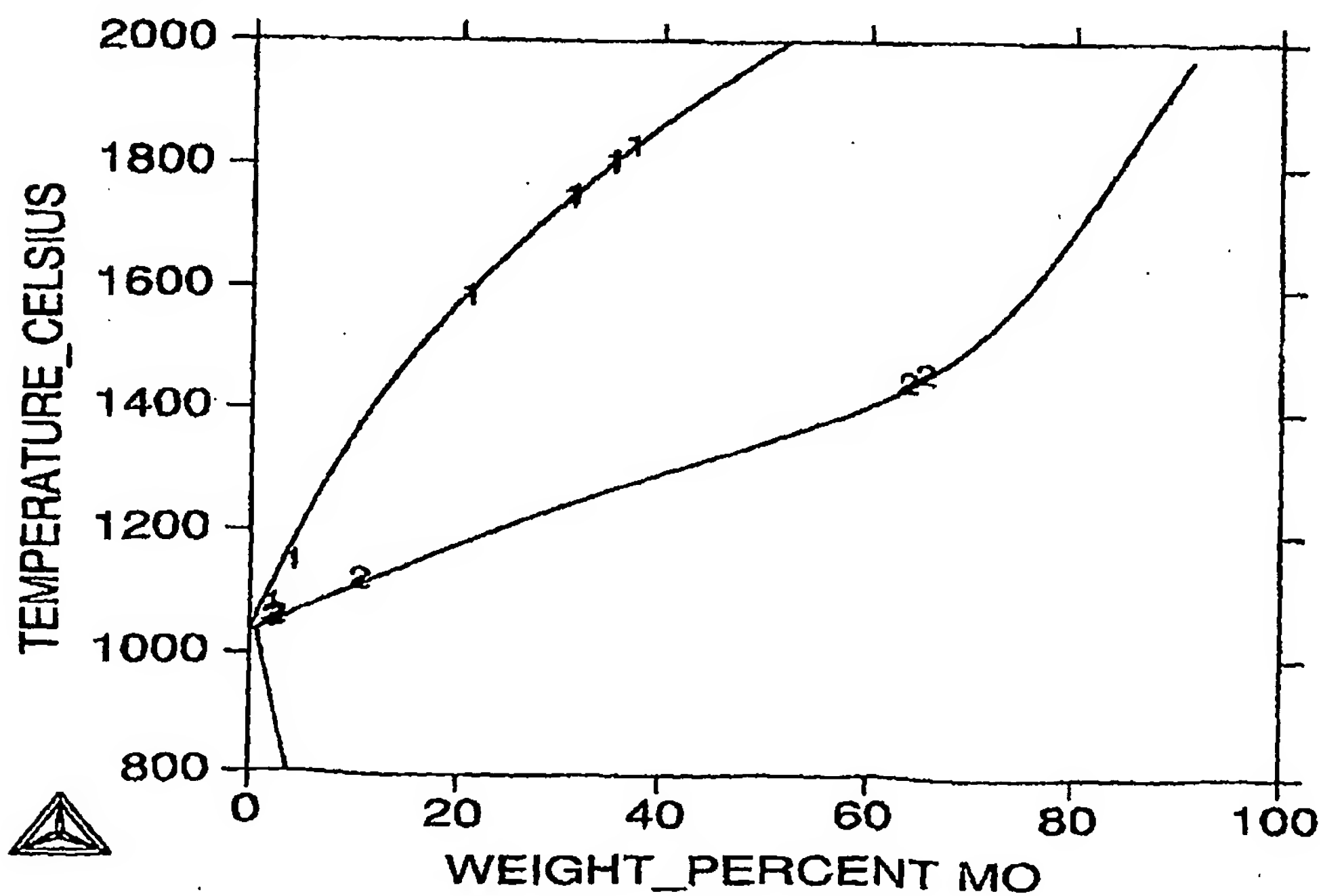


Figure 6



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Figure 7

